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NEW YORK UNIVERSITY

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University Heights, New York 53, N. Y.

**THE DISCREPANCY IN THE ROTATIONAL CONSTANTS
OF BROMOFORM**

Report No. 289.3

August 25, 1954

Low Frequency Absorption Project

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12. Abstract:

In the determination of the rotational constants of bromoform a large unexplained discrepancy was found between the results of Williams and Gordy working in the K-band and of Kojima et al. in the S-band. In the present experiment an attempt was made to repeat the S-band measurements of Kojima with a spectrometer having a greater sensitivity. This sensitivity has been verified by measurements on other molecules. No bromoform lines could be observed, and it must be concluded that they are too weak to be detected. Therefore the results of Kojima must be rejected as being due to some spurious effect.

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(Submitted for publication as a "Letter to the Editor"
in "The Journal of Chemical Physics")

The Discrepancy in the Rotational Constants of Bromoform*:

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In the determination of the rotational constants of bromoform (CHBr_3) a large unexplained discrepancy was found between the results of Williams and Gordy¹ working in the K-band region and of Kojima et al.² in the S-band region. The latter reported 32 lines in the frequency region 2450 - 2650 Mc/sec which were attributed to the fine structure of the $J = 0 \rightarrow 1$ rotational transition for the four common isotopic species of the molecule. In this investigation Kojima and his colleagues used an unmodulated spectrograph employing a double crystal circuit and oscilloscope presentation. The gas pressure used was 3 mm Hg with resulting poor resolution. The authors stated that their instrument had a sensitivity of $6 \times 10^{-8} \text{ cm}^{-1}$ while quoting the value $2 \times 10^{-8} \text{ cm}^{-1}$ as the intensity of an average line. Our own calculation, however, yielded the value $4 \times 10^{-10} \text{ cm}^{-1}$ for the intensity of the unsplit rotational line, or at most $1.5 \times 10^{-11} \text{ cm}^{-1}$ for the strongest individual fine structure component at room temperature. Part of this discrepancy may be due to the fact that we assigned to the line width the value of 20 Mc/sec per mm Hg while Kojima used the unusually small value of 1 Mc/sec per mm Hg, which enabled him in turn to claim good resolution in spite of the very high pressure. From the known line widths of similar molecules, our value seems to be the more reasonable one.

In order to verify Kojima's results a careful search was made in the region from 2200 to 2700 Mc/sec. The apparatus used consisted of a Stark modulated spectograph described elsewhere,³ which, owing to its very narrow band pass, we believe to be of considerable higher sensitivity than that employed by Kojima. As calculated by standard methods^{4,5} this sensitivity is about $1 \times 10^{-10} \text{ cm}^{-1}$, and this value was found to be consistent with observations made on other spectra with this apparatus.^{3,6} In spite of the greater sensitivity no lines attributable to bromoform were observed. We must therefore assume that bromoform lines in this region are too weak to be detected by presently available techniques.

This conclusion is supported by the recent work by Sterzer⁶ who, working in the same frequency region, was barely able to detect the $J = 0 \rightarrow 1$ spectrum of CF_3I . The similarity in structure and the proximity in frequency make possible a direct comparison of expected line intensity in bromoform and CF_3I which shows that individual bromoform lines should be much weaker. This is due primarily to the great complexity of the hyperfine structure which arises from presence of three bromine nuclei of spin $3/2$ and, in addition, the existence of four distinct isotopic species. In fact, more than 100 lines are predicted for the $J = 0 \rightarrow 1$ transition. In CF_3I the corresponding line splits into only three components. Furthermore the intensity CF_3I tends to be slightly greater because its rotational constants are larger. The bromoform spectrum is therefore so much weaker that detection appears highly improbable, if we consider that the CF_3I lines themselves are so near to the limit of observation.

We conclude therefore that the results obtained by Kojima et al.² must be rejected. The lines they report are undoubtedly due to some of the spurious effects which are frequently observed in microwave spectrographs.

While the present work has not yielded any positive support to Williams and Gordy¹, there appears no reason to doubt the validity of their work.

The writer wishes to thank Professor C. H. Townes of Columbia University, and Professor Yardley Beers of New York University for helpful discussions.

Footnotes

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